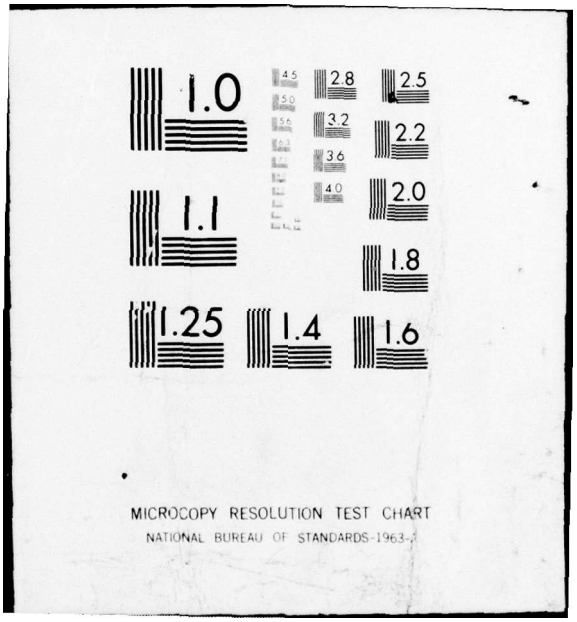
AD-A043 088 CALIFORNIA UNIV LOS ANGELES DEPT OF CHEMISTRY F/G 7/3
SYNTHETIC STUDIES WITH METALLOCARBORANES.(U)
APR 75 M F HAWTHORNE DA-ARO-D-31-124-72-G63

UNCLASSIFIED NL

| OF |
AD
A043088

END
DATE
FILMED
9-77
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
7.1
8.0
9.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

SYNTHETIC STUDIES WITH METALLOCARBORANES

FINAL TECHNICAL REPORT, 15 Dec 71-14 Dec 74

Principal Investigator: M. F. Hawthorne

15 December 1971 to 14 December 1974

16 Apr 75

ARO(D) Grant No.

DA-ARO-D-31-124-72-G63

126p.

Department of Chemistry
The University of California
Los Angeles, California

Approved for Public Release;
Distribution Unlimited.

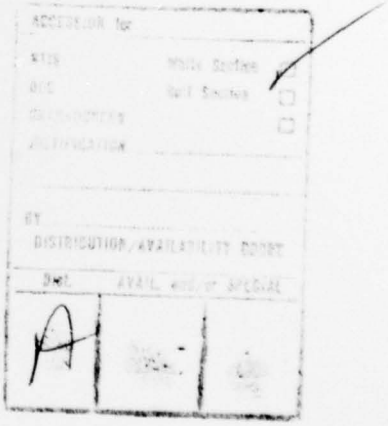
072255

During the contract period major advances along several related lines of research were made.

The polyhedral expansion reaction of carboranes was extended to 8, 9, 10 and 11 vertex species yielding the respective 9, 10, 11 and 12 vertex metallocarboranes of both cobalt and iron.[1] This reaction was also useful in producing bimetallic metallocarboranes.[2] Bimetallic and trimetallic metallocarboranes were also produced in the expansion of monometallocarboranes.[3,4,5,6]

The reaction of nucleophiles with metallocarboranes produced high yields of novel Lewis base adducts of nido metallocarboranes.[7] Thermal reactions of metallocarboranes, including migration of cobalt and carbon atoms[8,9] and thermal metal transfer reactions[10,11] were thoroughly explored and general rules governing these reactions were proposed.[8] In addition, electron counting rules for metallocarboranes were proposed,[12] defining electronic considerations for stable closo and nido species.

X-ray diffraction studies of several important metallocarboranes were performed confirming proposed structures for these species.[13,14,15]



PUBLICATIONS

1) W. J. Evans, G. B. Dunks and M. F. Hawthorne, "Synthesis of Metallocarboranes by Polyhedral Expansion," J. Amer. Chem. Soc., 95, 4565 (1973).

2) G. B. Dunks and M. F. Hawthorne, "The Non-Icosahedral Carboranes: Synthesis and Reactions," Accts. Chem. Res., 6, 124 (1973).

3) D. F. Dustin, W. J. Evans and M. F. Hawthorne, "The Synthesis of Cobaltaferracarboranes: Two Methods," J. Chem. Soc., Chem. Commun. 805 (1973).

4) W. J. Evans and M. F. Hawthorne, "Polyhedral Expansion of Metallocarboranes," Inorg. Chem., 13, 869 (1974).

5) W. J. Evans and M. F. Hawthorne, "The Synthesis of Fourteen-Vertex Metallocarboranes by Polyhedral Expansion," J. Chem. Soc., Chem. Commun., 37 (1974).

6) W. J. Evans and M. F. Hawthorne, "The Synthesis of a Trimetallic Metallocarborane by Polyhedral Expansion," Ibid., 706 (1973).

7) C. J. Jones, J. N. Francis and M. F. Hawthorne, "The Derivative Chemistry of Metallocarboranes. Nido-11-Atom Metallocarboranes and Their Lewis Base Adducts," J. Amer. Chem. Soc., 95, 7633 (1973).

8) W. J. Evans, C. J. Jones, B. Stibr and M. F. Hawthorne, "Rearrangements of Bimetallic Cobaltacarboranes," J. Organomet. Chem., 60, C27 (1973).

9) M. F. Hawthorne, K. P. Callahan and R. J. Wiersema, "Polyhedral Rearrangements Involving Five- and Six-Coordinate Carbon," Tetrahedron, 30, 1795 (1974).

10) W. J. Evans and M. F. Hawthorne, "Synthesis of Bimetallocarboranes by Thermal Metal Transfer," J. Amer. Chem. Soc., 96, 301 (1974).

11) W. J. Evans, C. J. Jones, B. Stibr, R. A. Grey and M. F. Hawthorne, "Polyhedral Metallocarborane Chemistry. Thermal Rearrangements of Bimetallic Cobaltacarboranes," Ibid., 96, 7405 (1974).

12) C. J. Jones, W. J. Evans and M. F. Hawthorne, "Electronic Considerations in Metallocarboranes," J. Chem. Soc., Chem. Commun., 543 (1973).

13) K. P. Callahan, F. Y. Lo, C. E. Strouse, A. L. Sims and M. F. Hawthorne, "Structures of Metallocarboranes. IV. Crystal and Molecular Structure of the Nido Metallocarborane Complex 8-η-Cyclopentadienyl-6,7-dicarba-8-cobalta-nido-nonaborane(11), 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$, at -160°," Inorg. Chem., 13, 2842 (1974).

14) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse and M. F. Hawthorne, "Structures of Metallocarboranes. V. Synthesis and Crystal and Molecular Structure of the Closo 20-Electron Bimetallocarborane 1,6-Bis(η-cyclopentadienyl)-1,6-diferra-2,3-dicarba-closo-decaborane(8), 1,6-(η-C_5H_5)$_2$-1,6.2,3-$Fe_2C_2B_6H_8$," J. Amer. Chem. Soc., 97 296 (1975).

15) F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler and M. F. Hawthorne, "Structures of Metallocarboranes. VI. A Titanium Sandwich Complex. Crystal and Molecular Structure of $[(CH_3)_4N]_2\{[1,6\text{-}C_2B_{10}H_{10}(CH_3)_2]_2Ti\}$, Bis-(tetramethylammonium) 4,4'-commo-Bis(decahydro-1,6-dimethyl-1,6-dicarba-4-titana-closo-tridecaborate)(2-) at -160°," Ibid., 97, 428 (1975).

The following scientific personnel were supported by this project during this reporting period:

William J. Evans, Ph.D., 1973

Frederick Lo, Graduate Student

James A. Doi, Graduate Student

Dr. C. J. Jones, Postdoctorate

Dr. Donald F. Dustin, Postdoctorate

Dr. William T. Scroggins, Postdoctorate

Respectfully submitted,

M. F. Hawthorne

April 16, 1975

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SYNTHETIC STUDIES WITH METALLOCARBORANES		5. TYPE OF REPORT & PERIOD COVERED Final 12/15/71 to 12/14/74 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. F. Hawthorne		8. CONTRACT OR GRANT NUMBER(s) DA-ARO-D-31-124-72-663
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of California, Los Angeles Los Angeles, California 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Box CM, Duke Station Durham, North Carolina 27706		12. REPORT DATE April 18, 1975 13. NUMBER OF PAGES 4
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metallocarboranes, Polyhedral expansion, cobaltacarboranes, ferracarboranes, cobaltaferracarboranes, X-ray diffraction.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The syntheses of mono-, bi- and tri-metallic metallocarboranes, and reactions of these materials are discussed. X-ray crystallographic data on several metallocarboranes is presented. Empirical rules governing rearrangement reactions and stability of metallocarboranes are also presented.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)